

CLAIMS

5 1. A catalyst for addition polymerisation of olefinically unsaturated monomers comprising:

*SH
B*
a) A first compound

MY

10 where: M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand.

Y is a monovalent divalent or polyvalent counterion;

15 b) An initiator compound comprising a homolytically cleavable bond with a halogen atom; and

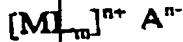
c) An organodiimine, where at least one of the nitrogens of the diimine is not part of an aromatic ring.

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2. A catalyst for addition polymerisation of olefinically unsaturated

monomers comprising:

d) A first component of Formula



where:

M = a transition metal of low valency state

L = an organodiimine where at least one of the nitrogens of the diimine is not a part of an aromatic ring.

A = an anion

n = an integer of 1 to 3

m = an integer of 1 to 2, and

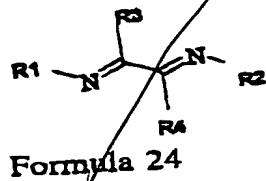
e) An initiator compound comprising a homolytically cleavable bond

with a halogen atom.

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2. A catalyst according to ~~any previous claim~~ wherein the organodiimine is selected from:

a 1,4-diaza-1,3-butadiene

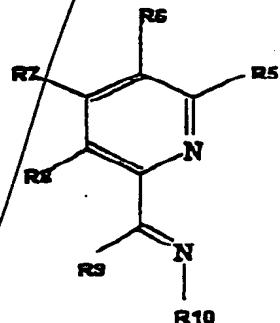


60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550 560 570 580 590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740 750 760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910 920 930 940 950 960 970 980 990 1000

A
S
B
20

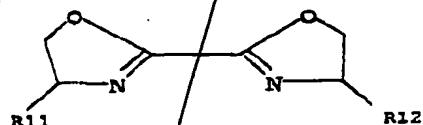
46

a 2-pyridine carbaldehyde imine



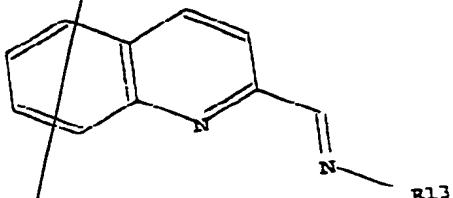
Formula 25

an oxazolidone



Formula 26

or a quinoline carbaldehyde



Formula 27

where:

R₁, R₂, R₁₀, R₁₁, R₁₂ and R₁₃ are independently selectable and may be selected from H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl, CH₂ Ar (where Ar is aryl or substituted) or a halogen;

15

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*S N
S P
C O*

R₁ to R₉ are independently selectable and may be selected from H, straight chain, branched chain or cyclic alkyl, hydroxyalkyl, carboxyalkyl, aryl, CH₂ Ar, a halogen, OCH_{2n+1} (where n is an integer of 1 to 20), NO₂, CN, O = CR (where R = alkyl, aryl, substituted aryl, benzyl PhCH₂, or a substituted benzyl).

5

B

*4. A catalyst according to claim 3 wherein R₁ to R₁₃ are selected from the group consisting of C₁ to C₂₀ alkyl, C₁ to C₂₀ hydroxyalkyl, C₁ to C₂₀ carboxyalkyl, n-propylisopropyl, n-butyl, sec-butyl, tert-butyl, cyclohexyl, 2-ethylhexyl, octyldecyl *and* lauryl.*

10

A

5. A catalyst according to claim 3 or claim 4, wherein the organodiimine comprises a chiral centre.

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b

*6. A catalyst according to claims 3 to 5 wherein one or more adjacent R₁ and R₂, R₃ and R₄, R₄ and R₅, R₁₀ and R₉, R₈ and R₉, R₈ and R₇, R₇ and R₆, R₆ and R₅ groups are selected from the group consisting of alkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl *and* cyclicaryl, containing 5 to 8 carbon atoms.*

B A

48 *Claim 1*

7. A catalyst according to ~~any previous claim~~ wherein M is selected from the group consisting of Cu(I), Fe(II), Co(II), Ru(II), Ni(II) Sm(II), Ag(I) and Yb(II).

A B 5

7. A catalyst according to ~~any of claims 1 and 3 to 7~~, wherein Y is selected from the group consisting of Cl, Br, I, NO₃, PF₆, BF₄, SO₄ and CF₃SO₃, CN, SPh, ScN and SePh.

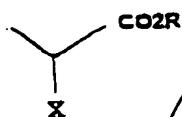
9. A catalyst according to ~~any of claims 2 to 7~~ wherein A is selected from Cl, Br, F, I, NO₃, SO₄ and CuX₂ (where X is a halogen).

8. 10. A catalyst according to ~~any previous claim~~, wherein the initiator is selected from:

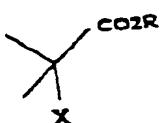
A

RX

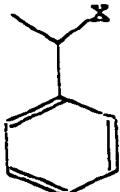
Formula 2



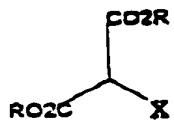
Formula 3



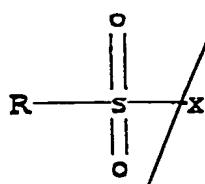
Formula 4



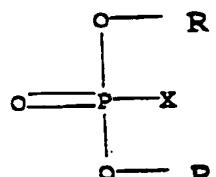
Formula 5



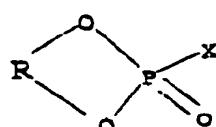
Formula 6



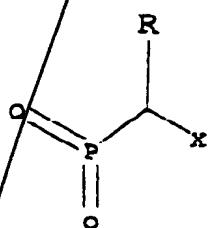
Formula 7



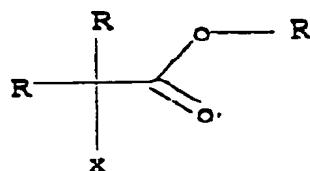
Formula 8



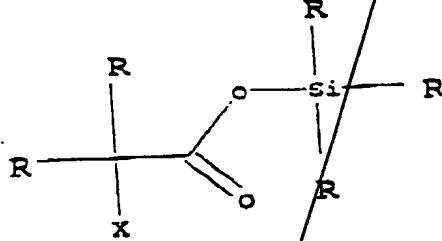
Formula 9



Formula 10



Formula 11

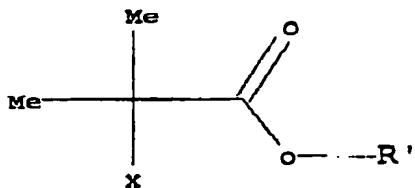


Formula 12

where R is independently selectable and is selected from straight chain alkyl, branched chain alkyl, cyclic alkyl, hydrogen, substituted alkyl, hydroxyalkyl, carboxyalkyl, aryl and substituted aryl and substituted benzyl.

X = a halide

⁹ 11. A catalyst according to claim ⁸ 10, wherein the initiator is



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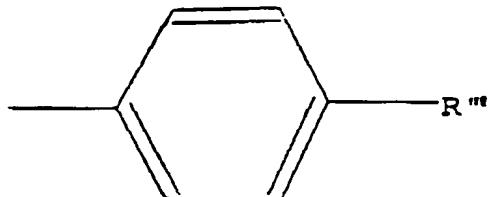
*wherein
where:*

B $X = \text{Br, I or Cl, preferably Br}$

B $R' = -\text{H,}$

B 10 $-(\text{CH}_2)_p\text{R}''$, (where p is a whole number and $\text{R}'' = \text{H, OH, NH}_2, \text{SO}_3\text{H, COOH, halide, COX, where X is Br, I or Cl},$)

or



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B $\text{R}''' = -\text{COOH, } -\text{COX, } (\text{where X is Br, I or Cl}), -\text{OH, } -\text{NH}_2 \text{ or } -\text{SO}_3\text{H.}$

B 12. ⁹ (b) A catalyst according to claim ¹¹ 10, wherein ^b is 2-hydroxyethyl-2'-bromopropionate.

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B 13. The use of a catalyst according to ~~any previous claim~~ in the

claim 1

*S
B
A*

addition polymerisation of one or more olefinically saturated monomers.

S N B 4 CM 5
 12
 14. The use of a catalyst according to claim 13 at a temperature between -20°C to 200°C.

A 10
 13
 15. The use of a catalyst according to claim 14 between 20°C and 130°C.

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14
 16. The use of a catalyst according to claims 13 to 15, wherein the olefinically saturated monomer is selected from methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), and other alkyl methacrylates; corresponding acrylates; also functionalised methacrylates and acrylates including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates; fluoroalkyl (meth)acrylates; methacrylic acid, acrylic acid; fumaric acid (and esters), itaconic acid (and esters), maleic anhydride; styrene, α -methyl styrene; vinyl halides such as vinyl chloride and vinyl fluoride; acrylonitrile, methacrylonitrile; vinylidene halides of formula $\text{CH}_2 = \text{C}(\text{Hal})_2$, where each halogen is independently Cl or F; optionally substituted butadienes of the formula $\text{CH}_2 = \text{C}(\text{R}^{13}) \text{C}(\text{R}^{15}) = \text{CH}_2$ where

R^{15} is independently H, C1 to C10 alkyl, Cl, or F; sulphonic acids or derivatives thereof of formula $CH_2 = CHSO_2OM$ wherein M is Na, K, Li, $N(R^{16})_4$, R^{16} , or $-(CH_2)_2-D$ where each R^{16} is independently H or Cl or C10 alkyl, D is CO_2Z , OH , $N(R^{16})_2$, or SO_2OZ and Z is H, Li, Na, K or $N(R^{16})_4$; acrylamide or derivatives thereof of formula $CH_2 = CHCON(R^{16})_2$, and methacrylamide or derivatives thereof of formula $CH_2 - C(CH_3)CON(R^{16})_2$. Mixtures of such monomers may be used.

17. The use of a catalyst, as defined in claims 1 and 3 to 12, according to claims 13 to 16, wherein the ratio (c):(a) is 0.01 to 1000 and the ratio of (a):(b) is 0.0001 to 1000.

18. The use of a catalyst as defined in claims 2 to 12 according to claims 13 to 16 wherein the ratio of Minitator is between 3:1 and 1:100.

19. The use of catalyst according to claims 13 to 16, where the polymerisation is undertaken in water, a protic or non-protic solvent.

20. The use of a catalyst according to claim 1 to produce a statistical copolymer, a block copolymer, a telechelic polymer or a comb and graft copolymer of monomers according to previous claim.

Add B6 >